The Anodic Oxidation of Methanol on
Raney-Type Catalysts of Platinum Metals

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1. INTRODUCTION

For a couple of years methanol has played an important
part in fuel cell research and development. It has proved
to be the only alcohol that can be completely oxidized to
carbon dioxide and water in a fuel cell operating with an
aqueous alkaline electrolyte at temperatures below 100°C and
a platinum catalyst (1). The disadvantage of a fuel cell
system of this type is the consumption of the alkaline elec-
trolyte due to formation of the carbonate. Therefore, acid
electrolytes would be more desirable; however, on platinum
the oxidation of methanol requires a much higher overvoltage
in acids than in alkaline solution.

It has been the objective of these investigations to
develop a suitable catalyst which does not require the large
overvoltage during the anodic oxidation of methanol. From
our previous investigations (2) it was concluded that there
might be a more active catalyst among the group of platinum
metals and their alloys and that the Raney method might be
suitable for preparation of alloy catalysts at low tempera-
tures.

2. EXPERIMENTAL CONDITIONS

In our comparative appraisal of the catalysts we used
electrodes of the type described in an earlier communication
(3). Accordingly, it contained the Raney catalyst in a gold
skeleton to which sodium chloride was added for formation of
macropores. The proportion of catalyst was kept constant
with all electrodes. The catalysts were prepared in situ
from Raney alloys of type $PtAl_4$ or $A_{0.5}B_{0.5}Al_4$ by treatment
with potassium hydroxide solution in the preformed electrode
disk. In separate experiments following the periodic poten-
tial sweep method the electrochemically active surface area
of the catalyst of such a test electrode was determined to be
about 35 sq.m. per g. in the case of platinum. X-ray dif-
fraction measurements for the example of the ruthenium-plati-
num catalyst showed a solid solution of ruthenium in platinum
which is not quite homogeneous but still contains proportions
of free ruthenium.

The electrolyte was 5 N potassium hydroxide solution and
4.5 N sulfuric acid (reagent grade: "pro analysi", E. Merck,
Darmstadt). In all experiments the methanol was used in a

concentration of c = 2 mole/liter (reagent grade of metha-
nol: "pro analysi", E. Merck, Darmstadt).

The electrochemical measurements were made in the half-
cell arrangement likewise described previously (3) according
to the galvanostatic method. The current densities reported
in this paper refer to the projected surface area and the
potential relates to a hydrogen electrode in the same solu-
tion. The ohmic drop between Luggin capillary and electrode
was not accounted for.

The plots were taken first at decreasing and then at in-
creasing current densities. This implies that a certain pro-
portion of the reaction products was present in the electro-
lyte.

3. RESULTS

3.1 Measurements in 6.5 N KOH Solution

Figures 1 and 2 show the differences in the catalytic
behavior of platinum metals in the oxidation of methanol in
5 N potassium hydroxide at 25°C and 80°C, respectively. Mea-
surements on electrodes with Raney gold serve for reference.

It is noted that two platinum metals at a time show a si-
milar activity. The three groups thus obtained conspicuously
correspond to the dyads

$$\text{Ru} \quad \text{Rh} \quad \text{Pd}$$
$$\text{Os} \quad \text{Ir} \quad \text{Pt}$$

of the platinum metals in the Periodic Table. Osmium and ru-
thenium, and also gold are found to be unsuitable as fuel cell
catalysts, since there will not be a constant potential at
high polarization. At 80°C, however, polarization with re-
spect to the potential at a current density of 50 mA/cm^2 which
is reasonable in fuel cell operation, does not exceed that mea-
sured on iridium and rhodium.

3.2 Measurements in 4.5 N Sulfuric Acid

3.2.1 Pure Platinum Metals

In sulfuric acid polarization with all platinum metals is
much larger than in potassium hydroxide solution. Particular-
ly striking is the increased polarization in the case of pal-
ladium at 25°C (Fig. 3), which even at comparatively small cur-
rent densities reaches a potential range where corrosion occurs.

Even at 80°C (Fig. 4) palladium shows only slightly lower
polarization so that this metal is the least active catalyst in
the conversion of methanol in sulfuric acid, whereas osmium,

featuring only low conversion at 25°C, is the most active
catalyst among the platinum metals. If the potential at
a current density of 50 mA/cm^2 is taken as a measure for
the "activity" of the electrode and thus of the catalyst,
the order at 80°C is as follows: Os > Ir = Ru > Pt > Rh > Pd.

In sulfuric acid the platinum metals do not form three
groups as has been observed in the conversion of methanol
in potassium hydroxide solution.

3.2.2 Alloys of Platinum Metals

The experimental results on pure platinum metals sug-
gest that catalysts of the lowest activity are found among
the palladium alloys. Figures 5 and 6 depict the potential/
current density curves of alloys of palladium with the ad-
dition of one of the other platinum metals (50 atomic per
cent).

A distinct increase in the activity is observed by the
addition of the second component. Worth noting is the ef-
fect of ruthenium which at a current density of 50 mA/cm^2
and 80°C (Fig. 5) results in a decrease in polarization by
280 mV and 25°C even causes a decrease by 300 mV (Fig. 6).
It should be borne in mind that pure ruthenium proved al-
most inactive at 25°C.

It now turns out that the most active catalysts are
found especially among alloys containing ruthenium (Figs. 7
and 8). A combination of pronounced activity is obtained by
a ruthenium-platinum alloy. At a current density of 50 mA/cm^2
and at 80°C (Fig. 7) such a Raney ruthenium-platinum elec-
trode shows a potential of 230 mV. Even at 25°C (Fig. 8) the
corresponding potential does not exceed 400 mV. These values
for the polarization are only about 50 mV higher than the
corresponding values for the most active catalyst in potas-
sium hydroxide solution, viz. platinum.

This Raney ruthenium-platinum catalyst is the most ac-
tive of all platinum metal alloys evaluated. This is il-
lustrated by Table 1 which summarizes the potentials of all
alloy catalysts of the composition A50B (atomic per cent) and
confronts them with those of the pure metals, as observed at
a current density of 50 mA/cm^2 and temperatures of 25°C (lower
values) and 80°C (upper values).

Next in the activity scale ranges the osmium-platinum
alloy. A very low activity at 80°C is registered not only
for palladium-gold but also for palladium-rhodium.

Our test electrode consisting of Raney ruthenium-platinum
on a gold skeleton enabled current densities of at least

5000 mA/cm^2 to be reached (Fig. 9), the potential remaining constant for extended periods of time. At a current density of 2000 mA/cm^2 the potential did not increase by more than 20 mV within 600 h (Fig. 10), provided that the concentration of methanol was kept approximately constant.

Ruthenium-platinum electrodes can also be used in the oxidation of methanol in a potassium bicarbonate electrolyte from which the resultant carbon dioxide gas escapes. Also in this case polarization is much lower than in the case of platinum as catalyst (Fig. 11).

Figure 12 shows the potential of electrodes with Raney platinum metal catalysts at 80°C and a current density of 50 mA/cm^2 as a function of the composition of the catalyst. It is worth noting that in most cases the potential reaches a minimum only with catalysts where the two components are present in about equal proportions, whereas in gas-phase reactions a synergistic effect is often caused even by minute additions. Attention is also called to the fact that an addition of rhodium to palladium hardly affects the potential within a comparatively wide range.

Discussion

The order of the activity of platinum metals in the oxidation of methanol in potassium hydroxide solution determined by our measurements is Pt > Pd > Ru = Rh > Ir > Os > Au and thus varies from the order Pd > Rh > Au > Pt reported in an earlier publication (4). Particularly striking is the extreme discrepancy in the case of platinum, which may possibly be explained by the fact that Tanaka (4) - in contrast to us - used the smooth metals. In addition, it has to be borne in mind that catalysts prepared by the Raney method contain aluminum in varying proportions (order of magnitude from 0.1 to 1 %), which may have a bearing on the activity.

In acid solutions, too, the order of the activity of platinum metals Os > Ru = Ir > Pt > Rh > Pd as determined by us varies from that reported by earlier authors (5). However, Breiter's values (5) are non-stationary values, since they were derived by the periodic potential sweep method. These measurements do not involve enrichment of intermediates in the electrolyte to such an extent as would always be encountered in fuel cell operation (6), (7).

Since the consecutive products of the oxidation of methanol continue to react at different rates in the presence of the different platinum metals, the enrichment varies from one metal to the other. Formic acid, for example, in contact with Raney platinum in alkaline electrolytes is oxidized more slowly than methanol, but more rapidly in the acid medium. In

contact with Raney palladium, on the other hand, formic acid
reacts at a higher rate than methanol even in the alkaline
electrolyte (3). Owing to this enrichment of the consecu-
tive products all methanol electrodes act as multiple elec-
trodes so that the measured potentials are mixed potentials.

Because of these difficulties there is still some doubt
about the oxidation mechanism of methanol, and this applies
even to platinum, a material often examined thoroughly in ex-
tensive investigations. The differences in the activity of
platinum metals in sulfuric acid as found by our measurements
encourage us to make the following speculations:

As the activity drops in the order Os > Ru = Ir > Pt > Rh
> Pd, the paramagnetic susceptibility of the metals qualita-
tively rises in almost the same order (cf. Table II); palla-
dium with the largest susceptibility value is the least active
catalyst.

Table II: Paramagnetic Susceptibility of Platinum Metals
$$(10^{-6} \text{ cgs})$$

Ru	Rh	Pd
43.2	111	567
Os	Ir	Pt
9.9	25.6	202

Since the paramagnetism of platinum metals results from
unpaired d-electrons - the very high value for palladium is
connected with quasi-ferromagnetic regions (8), (9) - it is
not unreasonable to assume a relationship between paramagnetic
susceptibility and catalytic activity.

Even for the activity of alloys of platinum metals such
a tendency can be qualitatively deduced: the addition of rho-
dium to palladium improves the activity but slightly up to
an amount of 50 at. %, whereas the addition of ruthenium has
a favorable effect (Fig. 12). With respect to susceptibility
(Fig. 13), the addition of small quantities of rhodium results
in a minor increase, and only additions of larger quantities
effect a decrease (10). Addition of ruthenium, even in low
concentrations, reduces the susceptibility significantly (11).

The synergistic effect on the anodic oxidation of metha-
nol observed with ruthenium-platinum alloys might be ascribed
to an optimum value of susceptibility leading to optimum sorp-
tion of all reactants. Since quantitative values for the para-
magnetic susceptibility of our alloys are not yet available,
the speculative nature of this statement is emphasized once
more. Evidence for relatively weak sorption is provided by

the fact that intermediates of the anodic oxidation of higher
or multivalent alcohols are desorbed by ruthenium-platinum
to such an extent that they condense to form brown-black pro-
ducts (12).

Hence, ruthenium-platinum alloys are almost specific for
the conversion of methanol and its consecutive products, but
these catalysts have also been found superior to platinum in
other reactions (13), (14). Even in the oxidation of metha-
nol the consecutive product - formaldehyde - is desorbed more
easily than in conversions on platinum so that in coulometric
measurements according to those described in (1) complete
conversion to carbon dioxide and water is not obtained at a
temperature of 80°C unless formaldehyde is not allowed to es-
cape (12).

In the meantime further references on the excellent pro-
perties of platinum-ruthenium catalysts in the anodic oxida-
tion of methanol have been mentioned (15). The catalyst de-
scribed in these publications has been prepared according to
Brown's method (16) by reduction of suitable salts with sodium
borohydride.

The experimental results available now show characteristic
differences among the binary alloys of the platinum metals as
concerns the activity in the anodic oxidation of methanol in
acid medium. Some reveal a synergistic effect whereas others
not even show an addition of the activity as a function of com-
position. This dissimilar behavior might be due to the dif-
ferences in the galvano-magnetic properties of the alloys. Fur-
ther data are necessary for a quantitative explanation of the
phenomena observed.

Acknowledgment

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2M CH_3OH
4.5N H_2SO_4, 80°C
50 ma/cm²

	Ru	Rh	Pd	Os	Ir	Pt	Au
Ru	350/≥900						
Rh	300/500	420/540					
Pd	290/490	520/580	570/800				
Os	290/≥900	320/540	340/720	320/880			
Ir	300/440	380/520	400/580	350/500	350/560		
Pt	230/400	330/510	480/610	250/440	290/490	370/540	
Au	310/≥900	460/580	650/780	400/≥900	300/540	380/580	≥900/≥900

Table I   Potentials at alloy catalysts (50 atomic %)
with methanol in 4.5 N H_2SO_4 at 25°C (lower
figures) and 80°C (upper figures); current
density: 50 ma/sq.cm.
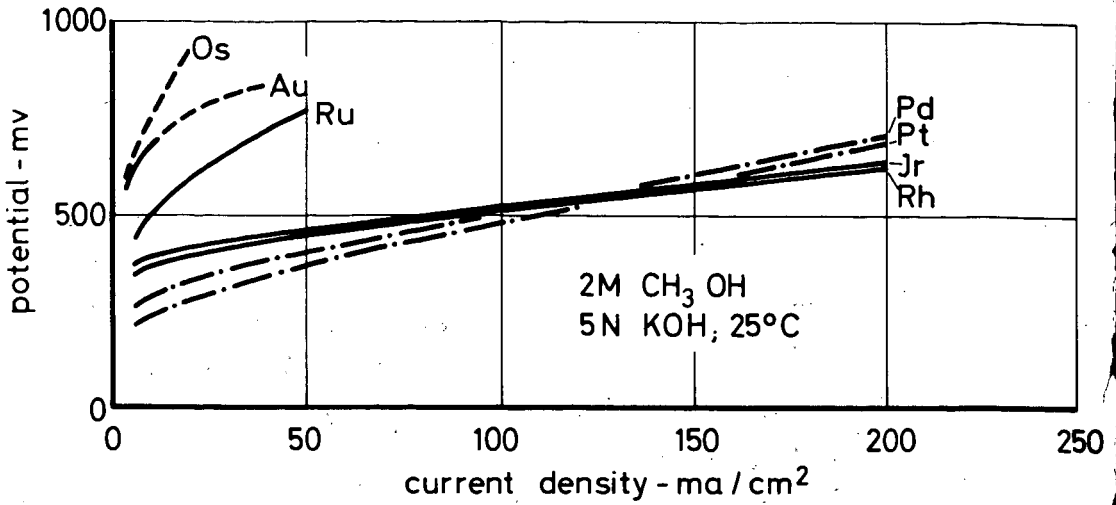
Fig. 1   Potential/current density plots of electrodes
          containing Raney platinum metals with methanol
          in 5 N KOH at 25°C
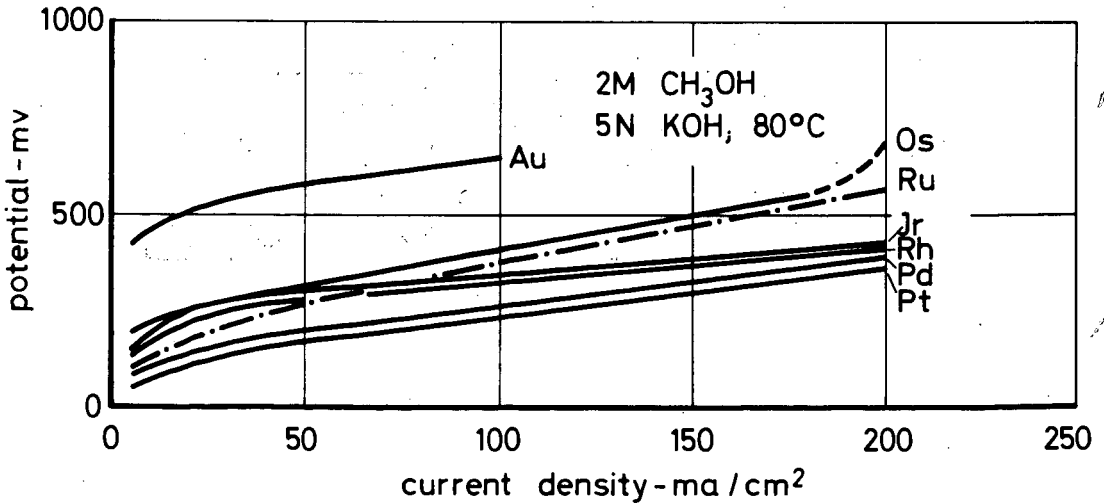
Fig. 2   Potential/current density plots of electrodes
          containing Raney platinum metals with methanol
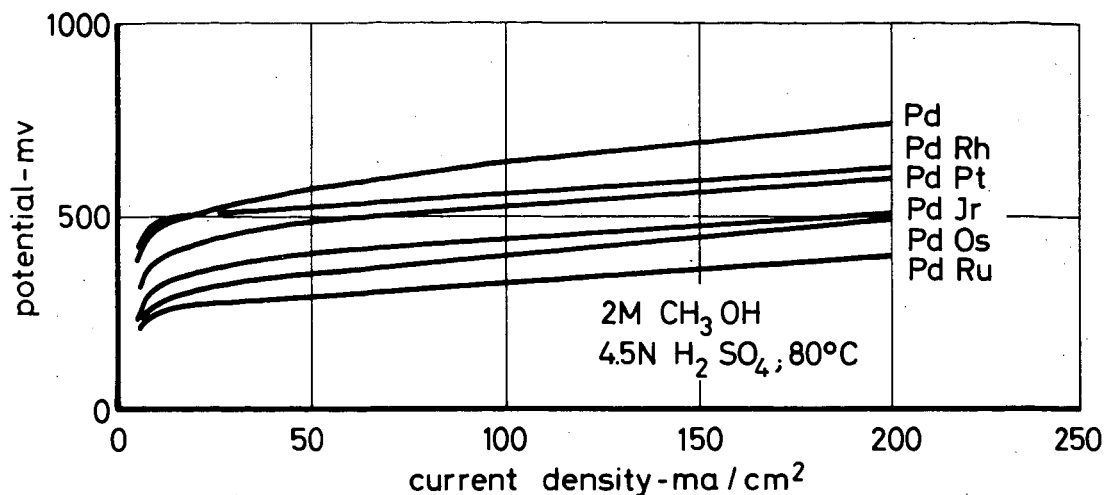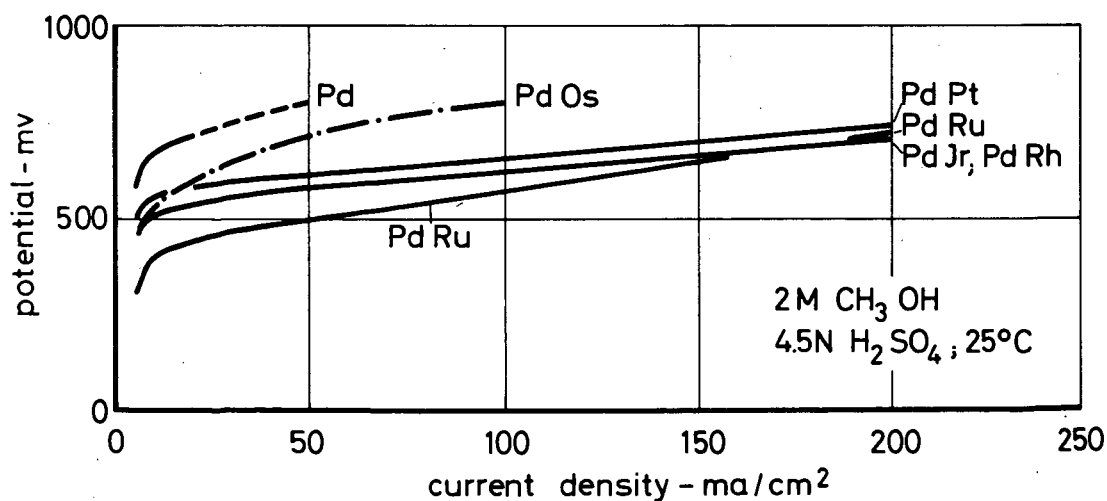   in 5 N KOH at 80°C
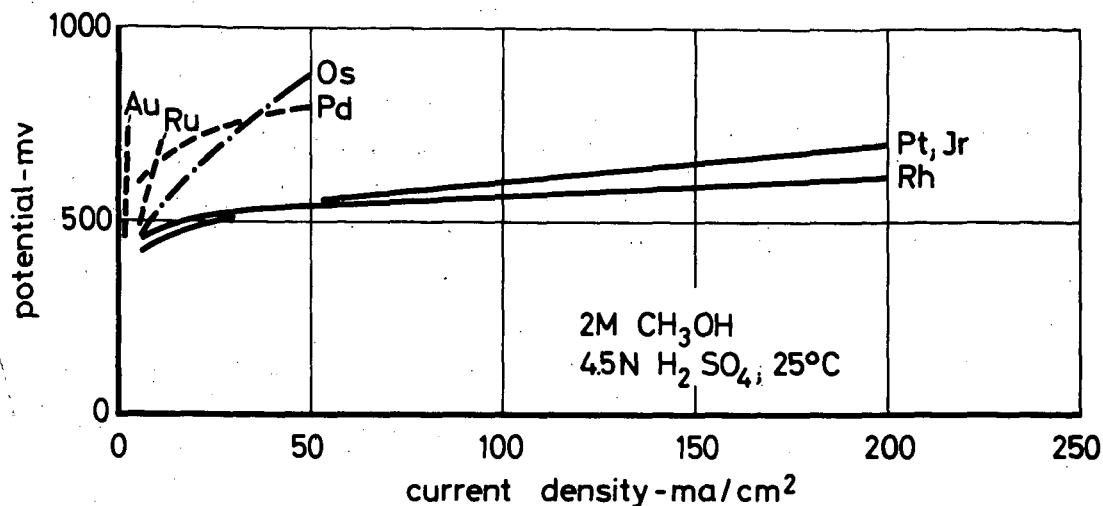
Fig. 3 Potential/current density plots of electrodes
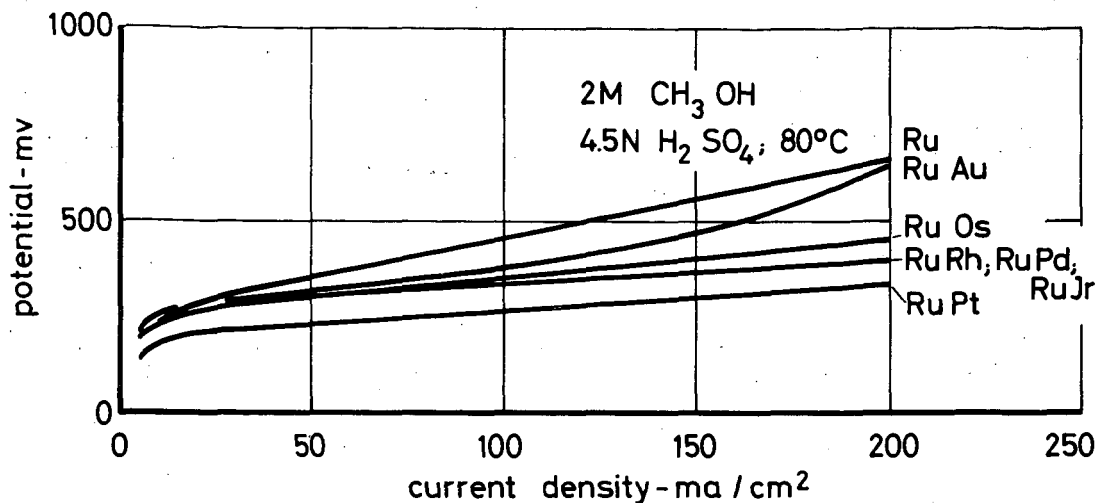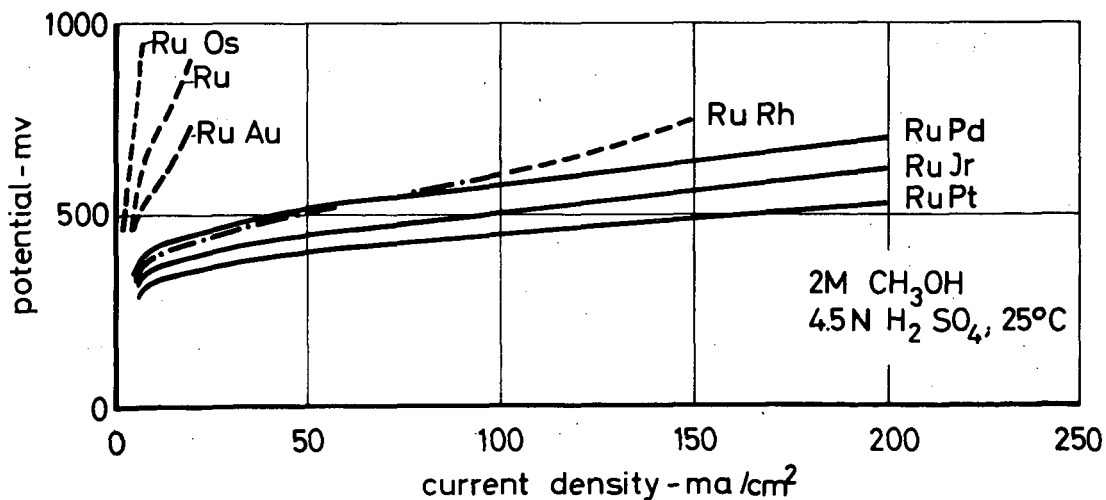containing Raney platinum metals with methanol
in 4.5 N H_2SO_4 at 25°C
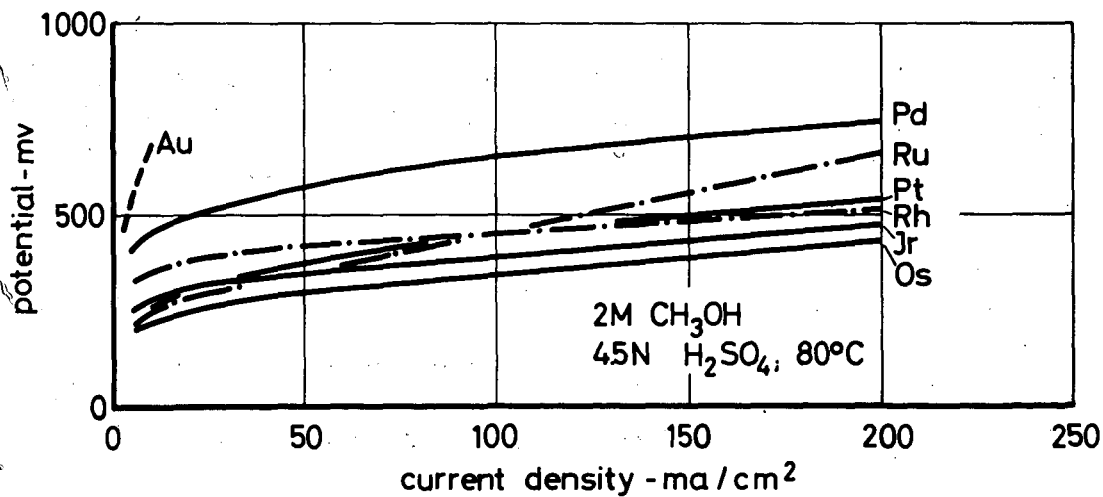
Fig. 4 Potential/current density plots of electrodes
containing Raney platinum metals with methanol
in 4.5 N H_2SO_4 at 80°C

Fig. 5   Potential/current density plots of electrodes
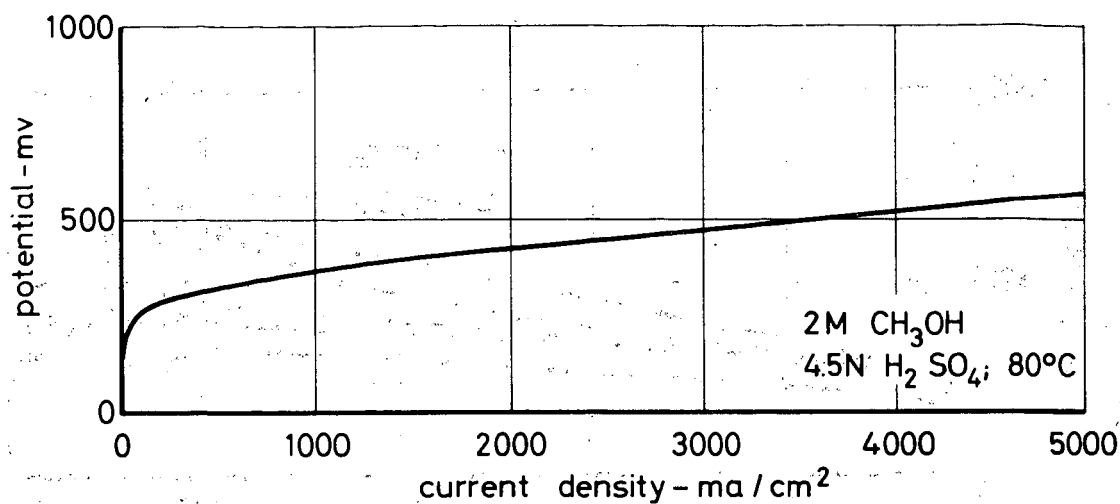containing Raney palladium alloys with methanol
in 4.5 N H$_2$SO$_4$ at 80°C

Fig. 6   Potential/current density plots of electrodes
containing Raney palladium alloys with methanol
in 4.5 N H$_2$SO$_4$ at 25°C

Fig. 7   Potential/current density plots of electrodes
containing Raney ruthenium alloys with methanol
in 4.5 N H_2SO_4 at 80°C

Fig. 8   Potential/current density plots of electrodes
containing Raney ruthenium alloys with methanol
in 4.5 N H_2SO_4 at 25°C

Fig. 9   Potential/current density plot of a Raney
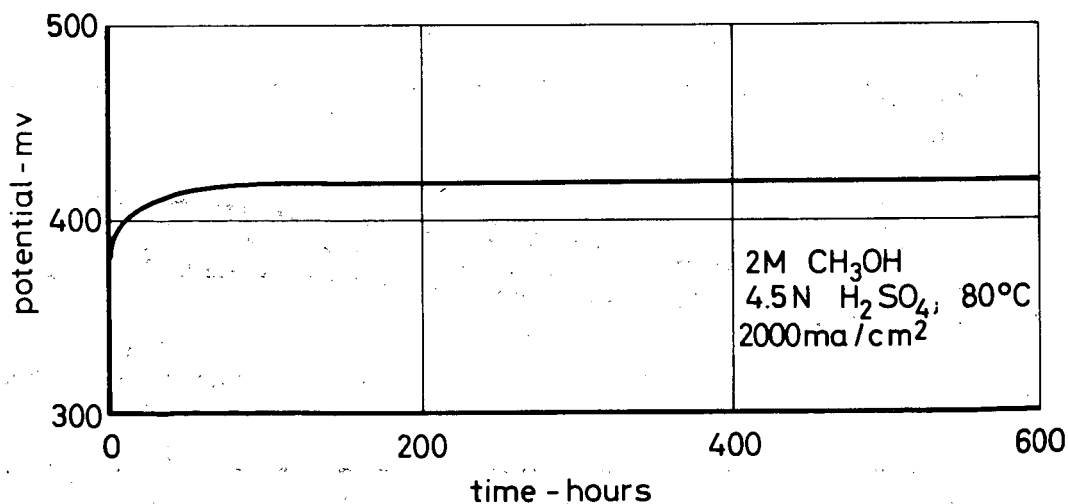   ruthenium-platinum electrode with methanol
          in 4.5 N H$_2$SO$_4$ at 80°C

Fig. 10   Change of potential with time on a Raney ru-
          thenium-platinum electrode with methanol in
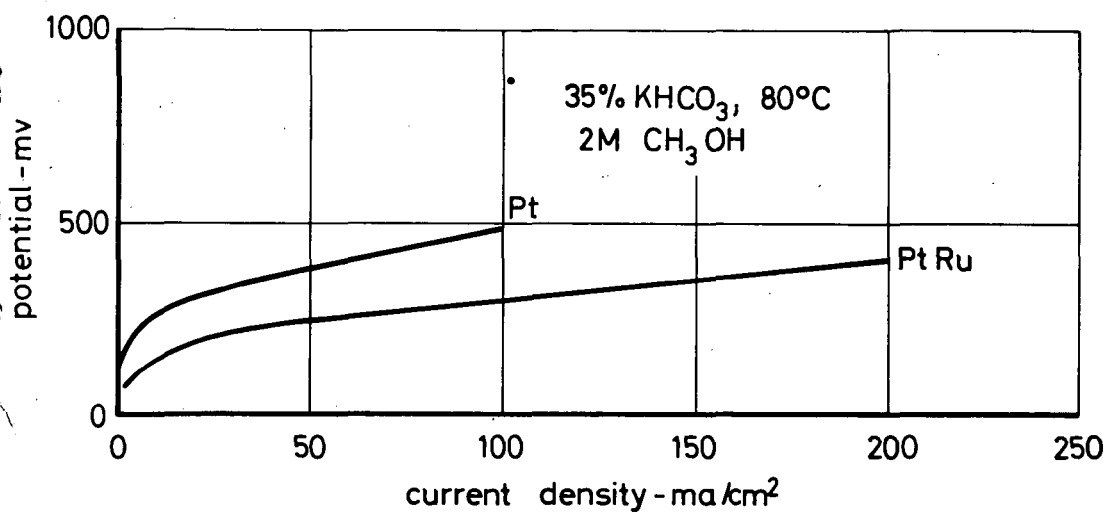   4.5 N H$_2$SO$_4$ at 80°C and a load of 2000 ma/sq.cm.

Fig. 11   Potential/current density plots of Raney
           platinum and Raney ruthenium-platinum with
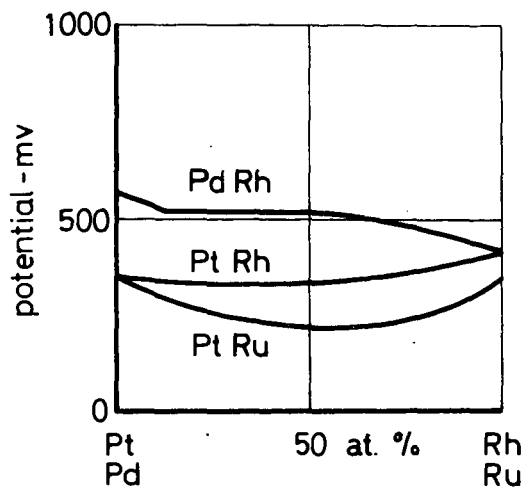   methanol in 35 % (by weight) KHCO$_3$ at 80°C

Fig. 12   Potential plots of platinum alloys with me-
           thanol in 4.5 N H_2SO_4 at 80°C as a function
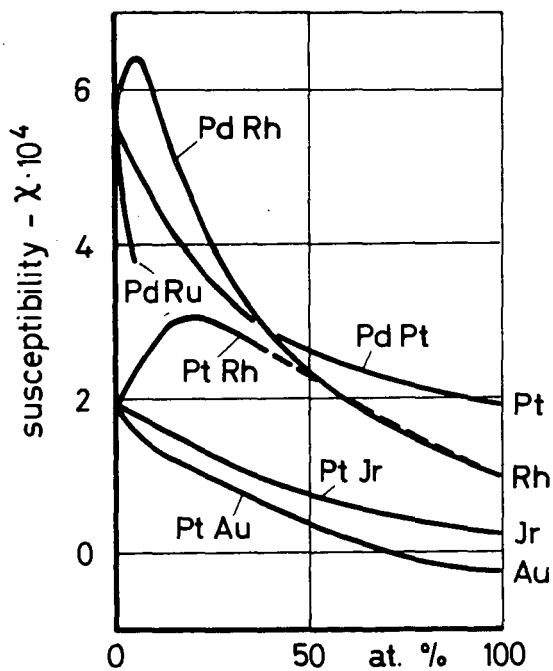   of composition

Fig. 13   Magnetic susceptibility of alloys of platinum
           metals as a function of composition (data from
           the literature)